FORMATION AND BEHAVIORS OF PHOTOTROP CENTERS IN GARNET CRYSTALS[1]

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ABSTRACT

As it is known the phototrop (PT) centers can be formed in chromium and divalent cations doped garnet crystals being grown in oxidation condition. No such centers can be formed if garnet crystals are grown in reduced conditions but they appear after sample has been annealed in oxidizing ambient atmosphere at high temperature. The present work pursues an object to study the mechanism of PT centers formation during thermal annealing under ionizing radiation influence and to clarify their spatial and electronic singularities in $Gd_3Sc_2Al_3O_{12}$ (GSAG) garnet crystals by investigation of their absorption and luminescent properties. As it turned out the thermal activated process of PT centers formation consists of two stages. At the first Cr^{3+} ions in octahedral sites turn into Cr^{4+} due to thermal diffusion of oxygen atoms through the crystal surface by the substitutional diffusion mechanism and then the redistribution of Cr^{4+} ions between octahedral and tetrahedral sites takes place. Both stages of PT centers formation process during the thermal annealing under ionizing radiation influence proceed at lower temperature. In the former case jumping oxygen ions can get the additional energy in the course of non-radiative recombination of radiation induced charge carriers so that during energy relaxation oxygen ions are able to accomplish considerably more number of jumps than in thermal condition only. In the latter case radiation lowering of potential barrier in consequence of radiation influence can cause the diffusion process to be far rapid. Destroying of chemical bounds near impurity cation may be a possible reason of barrier height lowering. Optical properties of γ-irradiated garnet crystals were investigated. Increasing of chromium concentration leads to improvement of the radiation hardness of garnet crystals.

KEY WORDS: diffusion; garnet crystal; ionizing radiation; phototrop centers;

1. INTRODUCTION

Among the numerous metal cations that can be incorporated into garnet crystals chromium ions are known [1,2] to form the phototrop (PT) centers. Usually Cr^{3+} ions substitute of any cations of octahedral (a) sites, while Cr^{4+} ions are incorporated into tetrahedral (d) sites. Just latter seem to be able to form PT centers. In particular, GSGG, GSAG YSAG garnet crystals when doped with chromium and divalent metals (Fe^{2+}, Ca^{2+}, Mg^{2+}) show an absorption band at 1 μm which can be brighten by 1.06 μm light for time interval of 5ns [2,3]. Moreover oxidizing ambient atmosphere is another necessary condition for Cr^{4+} centers formation. In the case of reduced atmosphere of crystal growth the charge compensation is realized by oxygen vacancies. The PT centers formation in such crystals can be realized by followed heat treatment at high temperature in oxidizing conditions. Due to difference of chromium ions optical properties in different neighbor surroundings garnet crystals are ideal model substances for the investigation of the thermodynamic equilibrium distribution of cations among nonequivalent lattice sites. Furthermore, these crystals provide an interesting possibility to study the kinetics of the cation redistribution process [4] and the involved ionic migration steps in solids [5].
All mentioned exceeds the framework of just academic problem but is of practice impotence. Both methods of PT centers creation by growing or heat treating in oxidizing atmosphere aren't free of defects. In former case the oxygen adding to inert atmosphere is pernicious for growing technique while in latter case undesirable large thermal stress upon crystal is possible to be expected. In this regard somehow lowering of ion migration activation energy for instance by radiation influence may allow decreasing the temperature of treatment.
Optical methods based on the measurement of absorption spectra related to the site occupancy of the chromium cations can be applied to determine the temperature dependence of cation distribution and redistribution for garnet system.
The present paper is concerned to study of thermal annealing and radiation simultaneous influence on the inter-sublattice site exchange of cations, process formation of PT centers and their properties in garnet crystals.

2. MEASUREMENTS

The investigated GSAG: Cr, Ca single crystals were grown by Czochralski method in different conditions. In one case, crystal A, ambient atmosphere consisted of H_2 (reduced conditions) while in another case, crystal B, the ambient atmosphere consisted of Ar with O_2 adding (oxidizing conditions). The chromium concentration was 5.10^{19}, 2.10^{20} and $3.10^{20} sm^{-1}$. The samples were cut from boules to the dimensions 10mm x 10mm x 1mm and polished to optical surface quality. Standard "Hitachi" EPS-3T model double beam spectrophotometer was used to measure optical absorption spectra at room temperature. Before the heat treatments were made absorption spectra were measured on each set of samples in the "as grown" state in the optical range 300-1300nm.
Two different procedures for heat treatment were applied to investigate the changes in the Cr cations distribution.

1. Both A and B samples were annealed in air atmosphere in the temperature interval from 700K to 1600K. After annealing time 1 hr at anneals temperature

the samples were cooled to room temperature. The samples annealed with this procedure are attributed to as heat- treated (HT) samples.

2. As grown sample A was fed into preheated at anneal temperature small furnace that was placed after that in radiation zone of ^{60}Co γ-source with a dose rate at the sample of about 4000R/s. After a holding time the furnace was removed from radiation zone and sample was quickly quenched to room temperature in air. The samples from this procedure are attributed to as heat - radiation treated (HRT) samples.

Each of experiment was performed during the same annealing time in air at controlled temperature. The garnet samples were placed into open Al_2O_3 ceramic container.
The thermal glow curves were taken by heating of samples prior irradiated to dose 10^6R at 77K.

3. RESULTS

Figure 1 presents for two different GSAG: Cr, Ca crystals the optical absorption spectra. The crystal A in "as grown" state showed two well resolved absorption bands peaking at 460 and 640nm (Fig. 1a, spectrum 1) due to well known optical transitions $^4A_2$— $^4T_1$ and $^4A_2$— $^4T_2$ of Cr^{3+} ion in a-site [6]. After annealing in air was performed a number of induced absorption bands peaking at 500, 660 and 1100nm was observed (Fig. 1a, spectrum 2). Initial spectrum of "as grown" GSAG: Cr, Ca crystal B reveals a very similar absorption bands (Fig.1b, spectrum 1). It should be noted, however, that the annealing in air followed just enhances the absorption bands mentioned (Fig.1b, spectrum 2). The appearing of absorption bands at 500, 660 and 1100nm is obviously in connection with oxidizing conditions during growth (sample B) or annealing (sample A). Earlier [7] it was pointed out that absorption band at 500nm can be induced in Cr doped YAG crystals under γ-irradiation or by annealing in oxidizing conditions and was ascribed as due to $^3A_2$ — $^2T_2$, $^1A_1$ transition of Cr^{4+} ion in octahedral site [8]. In our case an addition of Ca^{2+} ions substituting Gd^{3+} ions in c-sites needs of positive charge deficit compensation which is realized by oxygen vacancies formation in crystals A and by Cr^{4+} ions (and some quantity of oxygen vacancies) formation in crystals B. Due to oxygen ions diffusion into crystal body during annealing in oxidizing ambient oxygen vacancies concentration decrease takes place so that positive charge deficit compensation is realized owing to increase of Cr ions charge states. Absorption bands at 660 and 1100nm can hardly be related to Cr^{4+} ions in octahedral sites. At the same time in accordance with calculations within theory of crystal field these absorption bands can most likely be related to $^3A_2$ — $^3T_1$ and $^3A_2$ — $^3T_2$ transitions of Cr^{4+} ions in tetrahedron sites respectively [8]. There is sufficiently a good agreement between calculated and experimental data observed. It would be very tempting to explain the tetrahedral Cr^{4+}cenetrs formation by the same simple mode as in the case of octahedral Cr^{4+} centers i.e. by $Cr^{3+} \rightarrow Cr^{4+}$ conversion as result of oxidizing reaction. However, there is no evidence of the presence of Cr^{3+} ions in tetrahedral sites. Actually the occupation of a-sites by Cr^{3+} ions (ionic radius r =0,64A^o) during growth or annealing seems to be more probable because of Al^{3+}—O^{2-} distance for octahedral site is significantly larger than for tetrahedron one (1,84 and 1,76A^o respectively). The situation is quite different in the case of Cr^{4+} ion. Due to small size and $3d^2$ configuration electronic structure characteristic Cr^{4+} ions may occupy d-sites. The migration of cations from octahedral sites to tetrahedral ones in garnets at relatively low anneal temperature was proved to

occur in yttrium-iron garnets [9] and is connected with process migration activation energy decrease due to oxygen vacancies presence. The process of phototrop Cr^{4+} centers formation in GSAG:Cr,Ca crystals is supposed to be realized in sequence of events: oxidizing of Cr^{3+}ions in octahedral sites followed Cr^{4+}ions substitution into tetrahedral sites. At the same time oxygen vacancies seem to play a key role. It should be noted that phototrop Cr^{4+} centers never could be formed if any four charged cations (Si^{4+}, Ti^{4+}) are presented in the crystal. Such cations provide positive charge deficit compensation so that oxygen vacancy concentration is decreased.

In order to investigate the cation redistribution process more precisely, the temperature dependence of Cr^{4+} phototrop centers formation was studied. Figure 2 presents the change of optical density at 1100nm data vs the anneal temperature for two different treated crystals B. The number of salient features could be noted. In particular, one can clearly see that for HRT samples PT center formation process begins at significantly lower temperature than for HT samples. The same could be said in respect to PT centers saturation. Figure 3 shows the logarithm of the relative change of absorption coefficient vs reciprocal anneal temperature. One can see that dependence like $\log \Delta\kappa/\kappa \sim f(10^3/T)$ for both samples is different perceptibly in the range below 1000K: the slope of the line for HRT sample is considerably less than for HT one. It means the radiation component providing the decrease of activation energy of ions migration isn't described by Arrhenius activation process. Summarizing the aforesaid one can conclude that ionizing radiation gives rise to enhancement for PT centers formation in HRT samples. This includes the enhancement of both processes the Cr ions oxidizing as result of anion (oxygen) diffusion and the cation redistribution.

Oxygen atom diffusion into some garnet hosts was investigated (YAG [10], YIG [11]). The diffusion mechanism was determined to be substitutional diffusion i.e. jumping by the oxygen vacancies. The activation energy was obtained to attain about 3.0-3.5eV. The authors [10] reported that the diffusivity for oxygen thermal diffusion in YAG-Nd crystal increases in radiation field by a factor of 10^6. Among the possible mechanisms for diffusion activating in ionizing radiation field most preferable one seems to be due to as called θ- oscillations in solids [12]. Oxygen atoms from ambient atmosphere easily build in vacancies on the crystal surface and next diffuse into the crystal body by vacancies. The temperature dependence of diffusivity is described in terms of the usual diffusion equation:

$$D=D_0 \exp -E_D/kT. \quad (1)$$

Under irradiation oxygen atom traps free carrier (electron) and in the case of non-radiative recombination with opposite charge carrier it may get additional energy. In the course of surplus energy atom is able to accomplish considerably more jumps than during usual thermal diffusion. After all oxygen atom has reached the cation with variable valency (in our case Cr^{3+} ion) causes the oxidizing reaction:

$$Cr^{3+} + V_o + 1/2\ O_2 \rightarrow Cr^{4+} + O^{2-} \quad (2)$$

The cation charge state increasing and ionic radius diminution are the prerequisite for cation replacement into a site of less coordination number. The decrease of equilibrium temperature for cation redistribution under radiation influence may be due to reducing barrier height as a result of interaction of diffusible cation with holes localized in deep terms of host atoms. Such interaction causes the effective increasing of the number of jumps per time unit [13]. It is essential for realization this mechanism that diffusing

atom and local charge center should be placed in the immediate neighborhood. Such hole O^-- centers formation in garnet crystals under irradiation is mentioned in number of works (see [14,15]).
Another factor affecting the cation redistribution process under irradiation may be barrier height lowering as a result of interacting of impurity cations with intrinsic excitations arising in plenty under irradiation. The energy emitted during non-radiative dissociation of anion excitons or electron-hole recombination may lead to chemical bonds at the nearest surrounding of purity cation are broken.
The efficiency of mechanisms considered is depended on irradiation dose rate. Indeed preliminarily measurements revealed PT centers formation efficiency enhances versus γ-irradiation dose rate.
Susceptibility of Cr ions to change the charge state under irradiation may be a reason to PT centers' instability. To investigate the radiation stimulated PT's charge state transformation GSAG: Cr,Ca crystals B with different chromium concentration were selected. One can see in Fig.4 γ -irradiation decreases the intensity of absorption band at 1100nm in consequence of PT's centers damage as a result of electron trap: $Cr^{4+} + e^- \rightarrow Cr^{3+}$ (it is unlikely Cr^{5+} formation by means of hole trap). The main feature should be noted is decreasing of relative changing of PT's concentration with chromium concentration increasing. In particular when chromium concentration was 5.10^{19}, 2.10^{20} and $3.10^{20} sm^{-1}$ the damage of PT centers after γ-irradiation to 10^6R was amounted to 40, 10 and 5% at 300K and 70, 30 and 10% at 77K (Fig.5). Data obtained convince that "radiation hardness" of PT centers (electron traps) depends on thermal stability of a kind of hole centers. By another words the transformation of the deep hole centers into shallow ones should be happened when dopant concentration was increased. To clarify this suggestion thermal glow of GSAG:Cr, Ca crystals with different chromium concentration was measured. One can see in Figure 6 if dopant concentration has been increased the deep traps disappear whereas shallow ones appear. It is understandable now that deep center's disappearing exactly excludes recharged PT centers' stabilization at 300K. The fraction of Cr^{3+} ions in octahedral sites might be quite appropriate candidates as deep hole traps. As regarded shallow traps it is possible to suppose as a working hypothesis as follows. It is known that Cr^{3+}—Cr^{3+} double center formation in garnet crystals takes place if dopant concentration is increased [16]. The simultaneous localization of two holes on both cations is imagined to be improbable by the reason of strong Coulomb repulsion i.e. the number of deep hole centers is dropped off. At the same time the self-trapping of holes occurs in garnet lattice regular sites under γ-irradiation at temperature below 150K [17]. So that is why the relative changing of PT centers' concentration at 77K is significantly less than at 300K even chromium concentration is large.

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Figure Captions

Fig. 1. Optical absorption spectra of GSAG: Cr, Ca crystals grown in (a) H_2 and (b) Ar atmosphere. 1 - as grown; 2 - annealed in air at 1500K.

Fig. 2. Additional optical absorption at 1100nm of GSAG: Cr,Ca sample A annealed in air vs the anneal temperature. Squares refer to HT sample, triangles refer to HRT sample.

Fig. 3. The logarithm of additional absorption of GSAG: Cr,Ca sample A vs the reciprocal temperature.Squares refer to HT sample; triangles refer to HRT sample.

Fig. 4. Optical absorption spectra of PT center of GSAG: Cr,Ca crystals with chromium concentration (a) $5.10^{19}cm^{-3}$, (b) $2.10^{20}cm^{-3}$, (c) $3.10^{20}cm^{-3}$. 1 -as grown; 2 - γ-irradiated at 300K; 3 -γ-irradiated at 77K.

Fig. 5. Optical absorption coefficient at 1100nm of GSAG: Cr,Ca crystal vs chromium concentration.The sample was γ-irradiated at 300K (solid line) and 77K (dashed line).

Fig.6. The thermal glow of GSAG: Cr,Ca crystal with chromium concentration (a) $5.10^{19}cm^{-3}$, (b) $2.10^{20}cm^{-3}$, and (c) $3.10^{20}cm^{-3}$. The crystals were prior γ-irradiated to dose 10^6R at 77K.

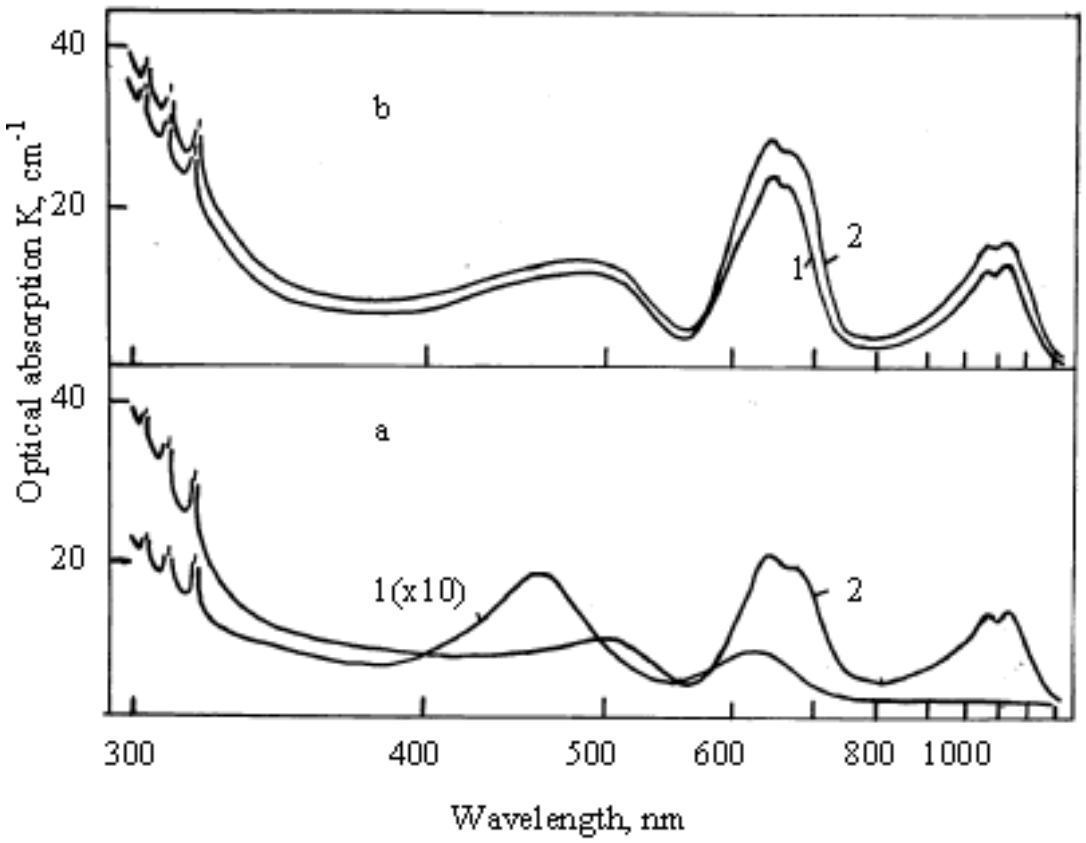
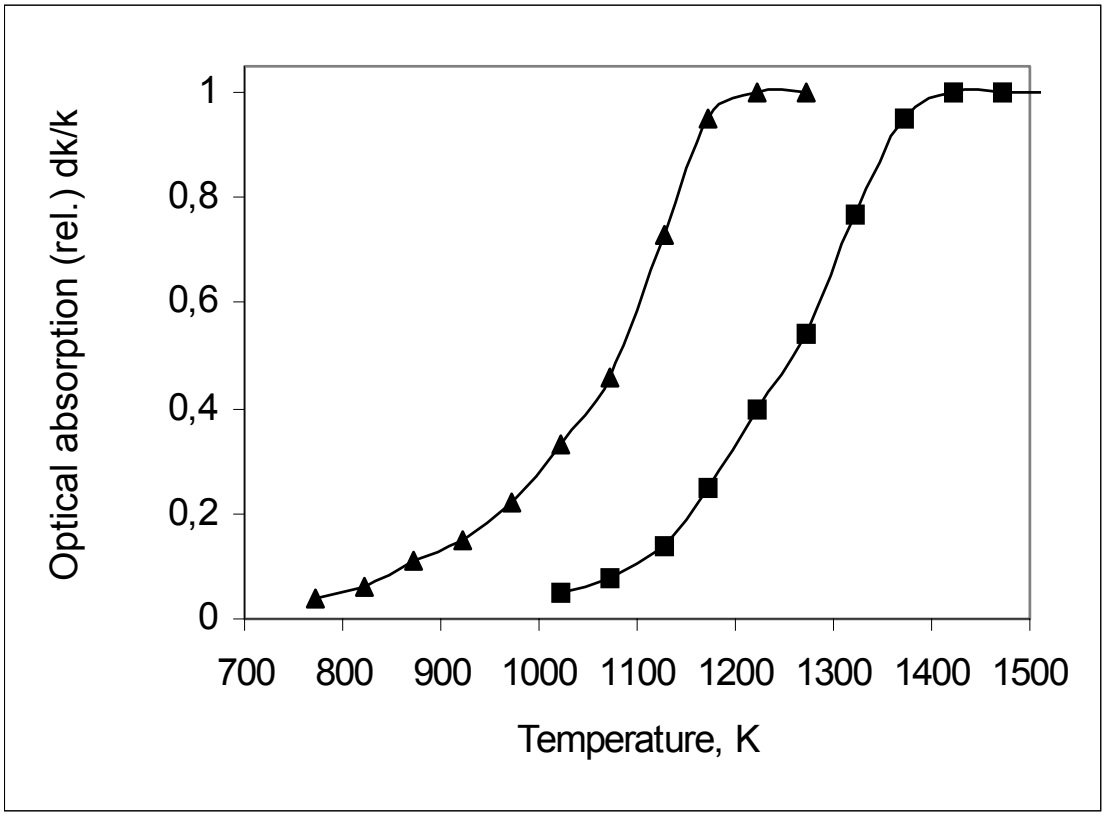

40
20
b
1
2
Optical absorption K, cm-1
40
20
a
1(x10)
2
300
400
500
600
800
1000
Wavelength, nm

Fig.1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0,4
0,2
0
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800
900
1000
1100
1200
1300
1400
1500
Temperature, K

Fig.2

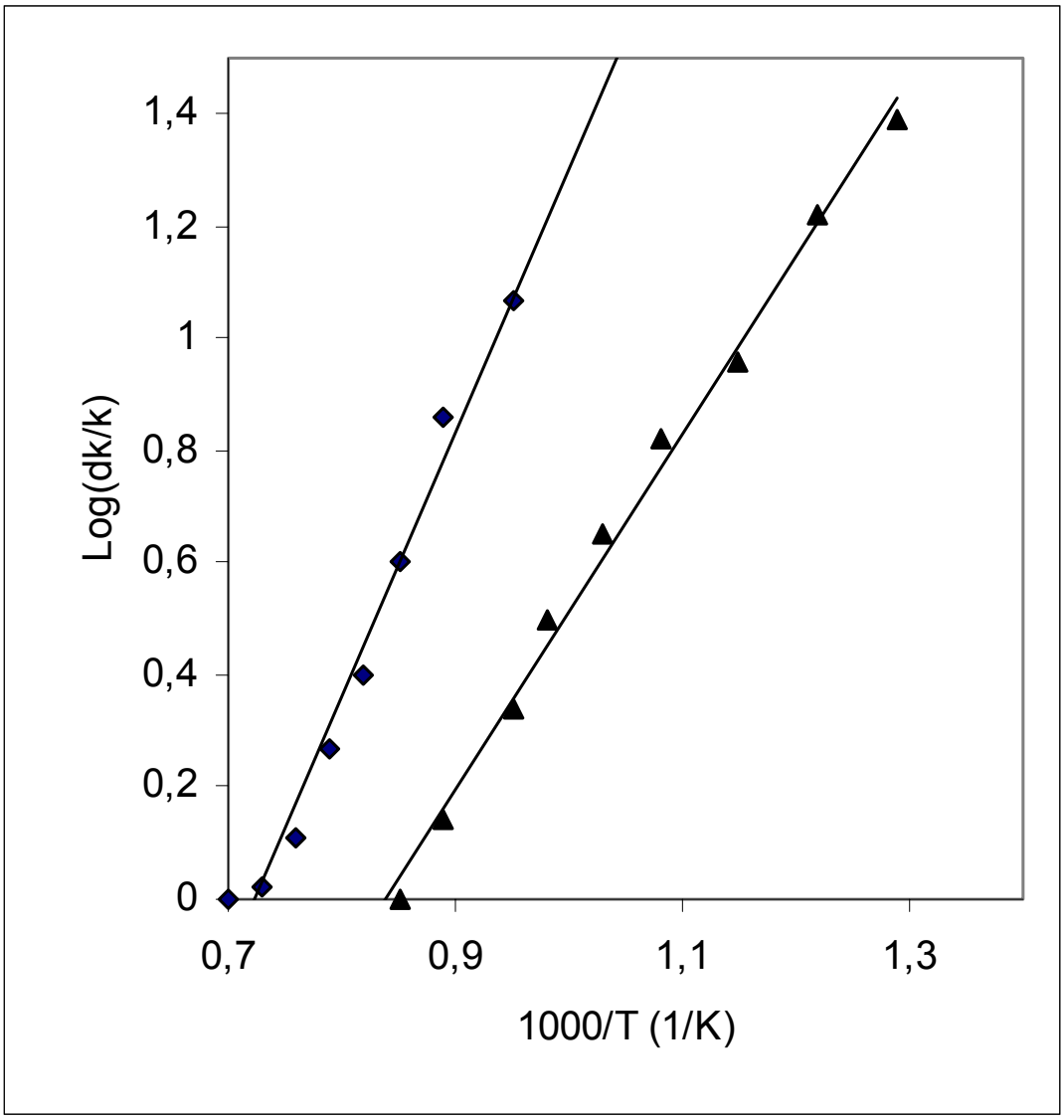
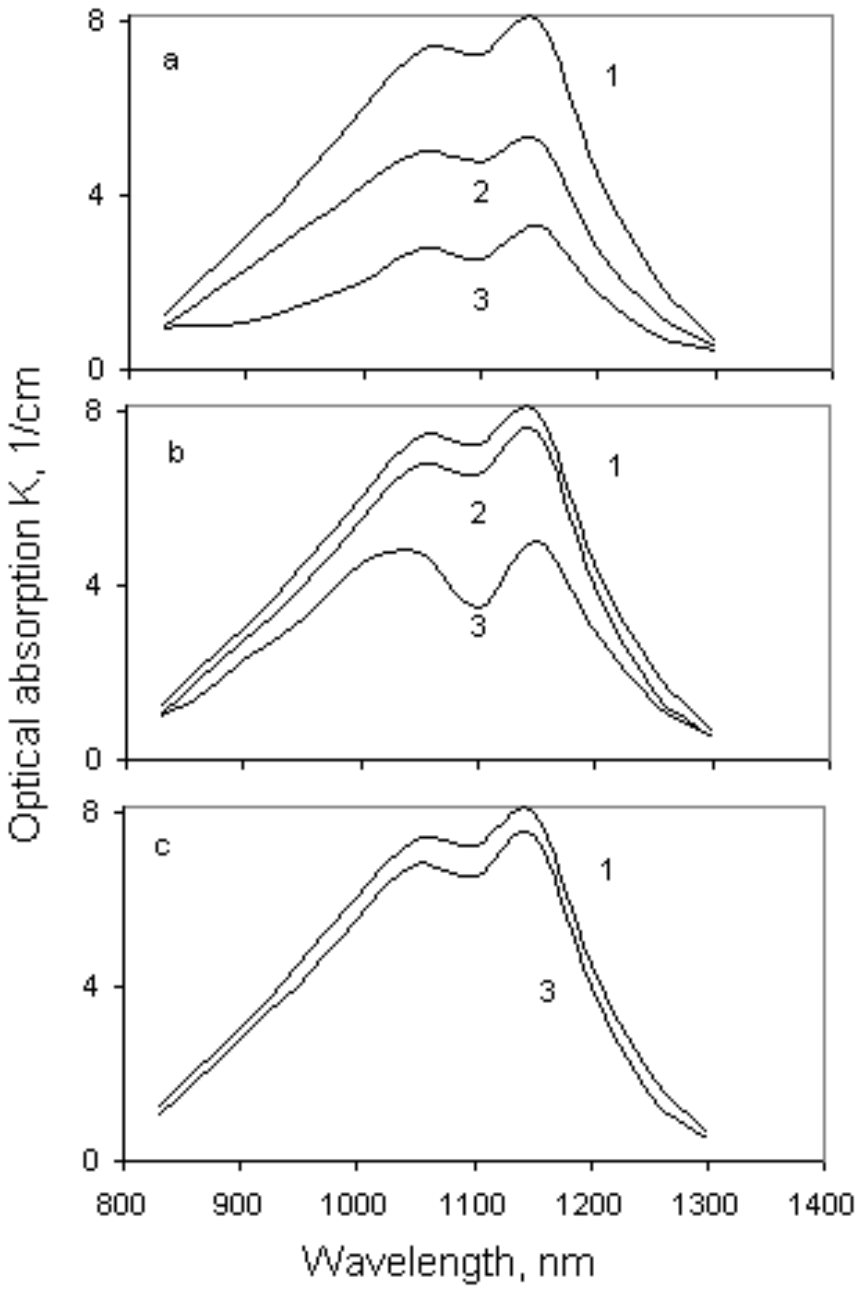


Fig.3


a
b
c
1
2
3
Optical absorption K, 1/cm
Wavelength, nm
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4
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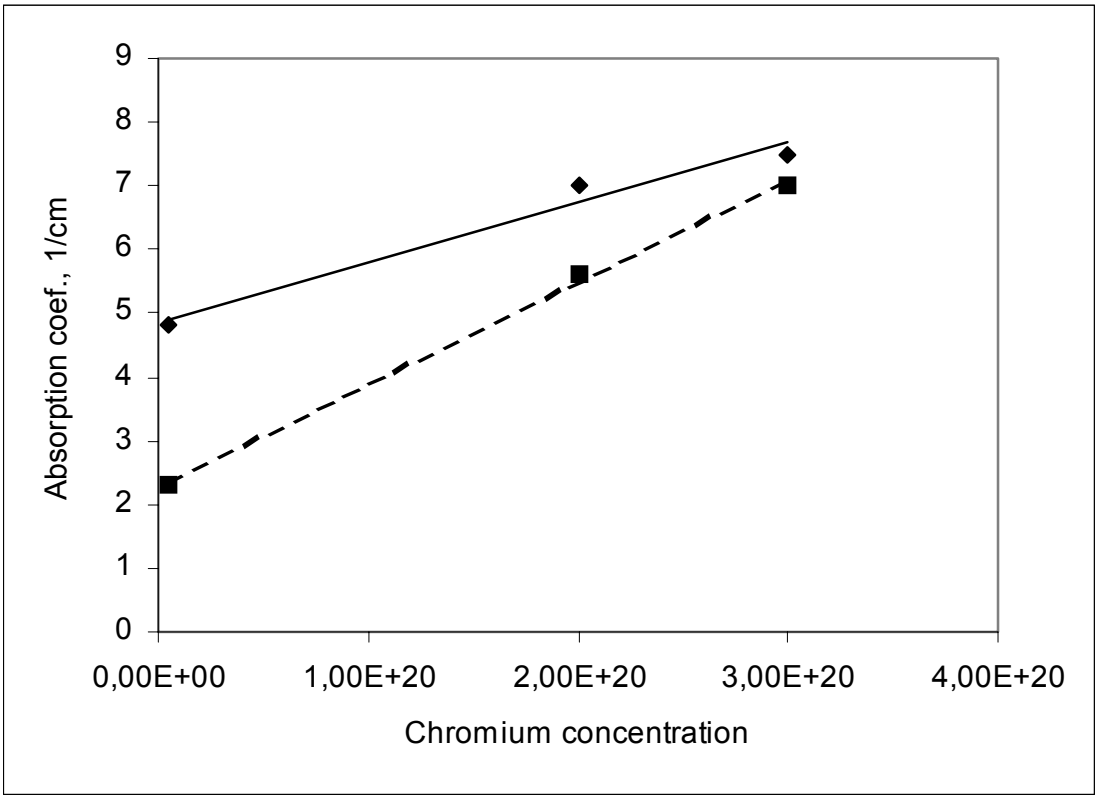
800
900
1000
1100
1200
1300
1400

Fig.4


9
8
7
6
5
4
3
2
1
0
Absorption coef., 1/cm
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2,00E+20
3,00E+20
4,00E+20
Chromium concentration

Fig.5

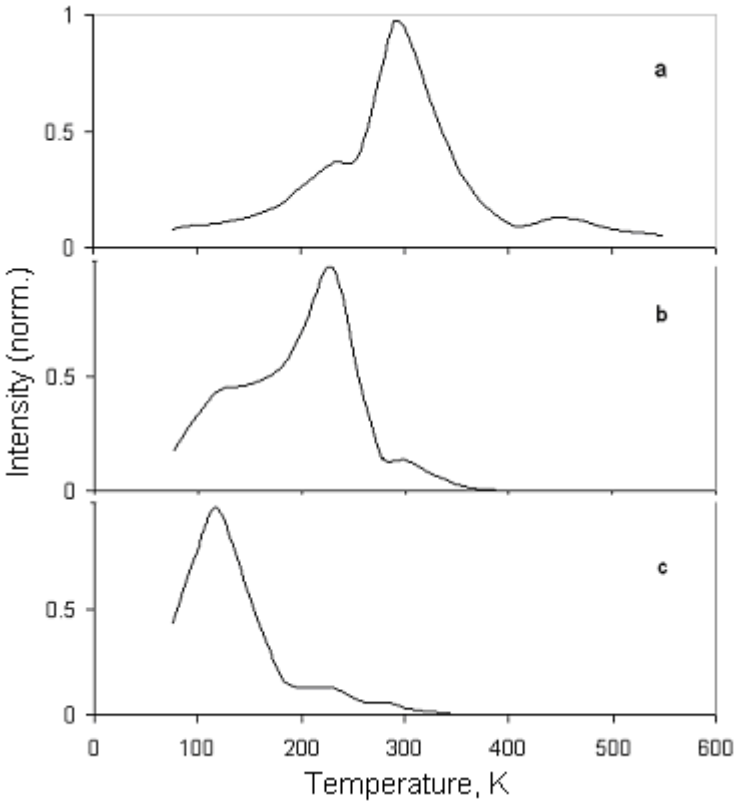
1
0.5
0
a
b
c
Intensity (norm.)
0
100
200
300
400
500
600
Temperature, K

Fig 6